Articles

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Syntheses, Electrochemistry, and Spectroscopic and Magnetic Properties of New Mononuclear and Binuclear Complexes of Vanadium(III), -(IV), and -(V) Containing the Tridentate Macrocycle 1,4,7-Trimethyl-1,4,7-triazacyclononane (L). Crystal Structures of [L₂V₂(acac)₂(μ-O)]I₂·2H₂O, [L₂V₂O₄(μ-O)]·14H₂O, and [L₂V₂O₂(OH)₂(μ-O)](ClO₄)₂

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The reaction of LVCl₃·dmf (1), where L represents the tridentate ligand 1,4,7-trimethyl-1,4,7-triazacyclononane (C₉H₂₁N₃) and dmf is dimethylformamide, with CF₃SO₃H yields the very reactive green complex LV(O₃SCF₃)₃ (2), which is a useful starting material for the synthesis of a variety of mononuclear and binuclear complexes of vanadium. Thus, 2 reacts under anaerobic conditions with NaSCN affording LV(NCS)₃ (3) and with NaN₃ in the presence of air affording LVO(N₃)₂ (4). Hydrolysis of 2 under anaerobic conditions in the presence of NaOCN yields the oxo-bridged, purple binuclear species [L₂V₂(OCN)₄(μ-O)]·2H₂O (6) whereas in the presence of O₂ the reaction yields LVO(NCO)₂ (5). Hydrolysis of 1 with acetylacetonate (acac) affords upon addition of NaI purple crystals of [L₂V₂(acac)₂(μ-O)]I₂·2H₂O (7), the structure of which has been determined by X-ray crystallography: space group *P*2₁/*n*; *a* = 9.078 (6), *b* = 12.785 (8), *c* = 16.96 (1) Å; β = 99.93 (5)°; *Z* = 2. The same reaction carried out in the presence of sodium benzoate affords green crystals of [L₂V₂(μ-O)(μ-O₂CPh)₂]I₂·H₂O (8). Two binuclear complexes of vanadium(V) have also been synthesized: [L₂V₂O₅]·14H₂O (9) is synthesized from NH₄VO₃ (or V₂O₅) and the ligand L in a CH₃CN/H₂O mixture. 9 is readily protonated in acidic media, yielding yellow crystals of [L₂V₂O₂(OH)₂(μ-O)](ClO₄)₂ (10). The crystal structures of 9 and 10 have been determined by X-ray crystallography. Crystal data for 9: space group *P*2₁/*c*; *a* = 10.587 (3), *b* = 8.608 (2), *c* = 23.049 (4) Å; β = 115.74 (2)°; *Z* = 2. Crystal data for 10: space group *P*2₁/*n*; *a* = 8.762 (3), *b* = 13.975 (5), *c* = 11.988 (3) Å; β = 101.23 (3)°; *Z* = 2. Spectral (UV–vis) and magnetic properties of new complexes are described; the electrochemistry has also been investigated.

Introduction

In this paper we report the preparation and characterization of three new binuclear complexes containing the [V^III–O–V^III]⁴⁺ unit. Complexes of this type have been known to exist in acidic aqueous solution as intermediates in the oxidation of V(II) by vanadyl complexes.[2–5]

$$V^{2+} + VO^{2+} \rightarrow [V^{III}-O-V^{III}]^{4+} + 2H^+ \rightarrow 2V^{3+} + H_2O$$

To date, only a few species have been isolated as crystalline materials, and only three complexes have been characterized by X-ray crystallography: [(THF)₃Cl₂VOVCl₂(THF)₃],[6] [V₂O(SCH₂CH₂NMe₂)₄],[7] [L₂V₂(μ-O)(μ-O₂CCH₃)₂]I₂·2H₂O (L = 1,4,7-trimethyl-1,4,7-triazacyclononane).[8] Na₂[V₂O(ttha)]·dmf·3H₂O (ttha = triethylenetetraminehexaacetate(6–))[9] has been isolated, but its structure has not been determined. The first two complexes have a linear [V–O–V]⁴⁺ core of type A whereas the third compound contains a bent [V–O–V]⁴⁺ unit of type B. More common and structurally better characterized are trinuclear
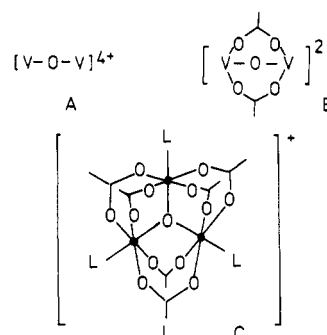

compounds of type C containing the well-known triangular oxo-centered core M₃O(RCO₂)₆L₃; a number of vanadium(III) complexes of this type have been reported in the literature.[10–12]

While the spectroscopic properties of these compounds have been reported in some detail, their magnetic properties have not been thoroughly investigated. The nature of the spin-exchange coupling within the [V–O–V]⁴⁺ unit, if it then exists, is of considerable interest. We have, therefore, measured the magnetic susceptibility as a function of temperature in the range 10–300 K of a new complex of type A and one of type B. In both cases considerable intramolecular ferromagnetic spin-exchange coupling has been observed. Christou reports[7] that at room temperature

(1) (a) Ruhr-Universität. (b) Universität Heidelberg. (c) Universität Kaiserslautern.
(2) Biermann, W. J.; Wong, W.-K. *Can. J. Chem.* 1963, *41*, 2510.
(3) Newton, T. W.; Baker, F. B. *Inorg. Chem.* 1964, *3*, 569.
(4) Newton, T. W.; Baker, F. B. *J. Phys. Chem.* 1964, *68*, 2.
(5) Gandeboeuf, J.; Souchay, P. *J. Chim. Phys. Phys.-Chim. Biol.* 1959, *56*, 358.
(6) Chandrasekhar, P.; Bird, P. H. *Inorg. Chem.* 1984, *23*, 3677.
(7) Money, J. K.; Folting, K.; Huffman, J. C.; Christou, G. *Inorg. Chem.* 1987, *26*, 944.
(8) (a) Wieghardt, K.; Köppen, M.; Nuber, B.; Weiss, J. *J. Chem. Soc., Chem. Commun.* 1986, 1530. (b) Köppen, M.; Fresen, G.; Wieghardt, K.; Llusar, R. M.; Nuber, B.; Weiss, J. *Inorg. Chem.* 1988, *27*, 721.
(9) Myser, T. K.; Shepherd, R. E. *Inorg. Chem.* 1987, *26*, 1544.

(10) Cotton, F. A.; Lewis, G. E.; Mott, G. N. *Inorg. Chem.* 1982, *21*, 3127.
(11) (a) Cotton, F. A.; Lewis, G. E.; Mott, G. N. *Inorg. Chem.* 1982, *21*, 3316. (b) Cotton, F. A.; Extine, M. W.; Falvello, L. R.; Lewis, D. B.; Lewis, G. E.; Murillo, C. A.; Schwotzer, W.; Tomas, M.; Troup, J. M. *Inorg. Chem.* 1986, *25*, 3505.
(12) (a) Cannon, R. D.; White, R. P. *Prog. Inorg. Chem.* 1988, *36*, 195. (b) Jezowska-Trzebiatowska, B.; Pajdowski, L. *Rocz. Chem.* 1958, *32*, 1061. (c) Allin, B. J.; Thornton, P. *Inorg. Nucl. Chem. Lett.* 1973, *9*, 449.

Scheme I
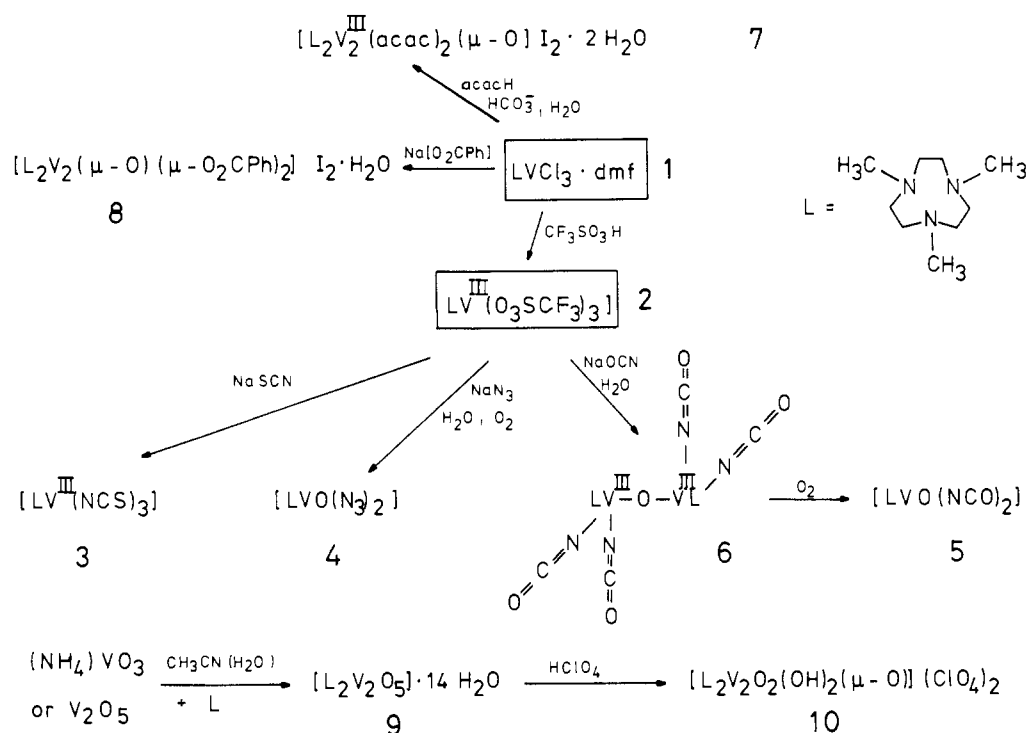
his complex [V₂O(SCH₂CH₂NMe₂)₄] exhibits the spin-only magnetic moment for each V(III) center, which implies the lack of intramolecular ferro- or antiferromagnetic coupling. Complexes of type C also show no coupling,[12] although precise low-temperature magnetic susceptibility data are lacking.

In the second part of this paper we describe the synthesis, structural characterization, and reactivity of a binuclear vanadium(V) complex containing the hitherto unknown [V₂O₅] core[13] where two *cis*-dioxovanadium(V) units are bridged by one oxo ligand. The [M₂O₅]²⁺ core is well-known in molybdenum(VI) chemistry,[14] and it has recently been structurally characterized in [L₂W₂O₅](S₂O₆)·4H₂O, a binuclear tungsten(VI) complex.[15] Floriani and co-workers have drawn analogies between the *cis*-VO₂ group and organic carboxylates.[16] Thus, the VO₂⁺ group may be protonated, yielding VO(OH)²⁺ (the analogue of a carboxylic acid), or "esterified", affording VO(OR) species.[17] Pecoraro and co-workers have recently characterized the protonated [VO(OH)(HSHED)]⁺ and deprotonated VO₂(HSHED) complexes, but the former has not been isolable as solid (HSHED is the monocation of *N*-salicylidene-*N'*-(2-hydroxyethyl)ethylenediamine).[30] In nice agreement with this concept we have found that [L₂V₂O₅] is easily protonated in acidic aqueous solution. The crystal structure of the product [L₂V₂O₂(OH)₂(μ-O)](ClO₄)₂ has been determined, and the protonation sites at two terminal oxygen atoms have been unambiguously established for the first time.

Scheme I displays the synthetic routes to the new complexes described in this paper and gives their labels used in this paper. In order to synthesize binuclear oxo-bridged transition-metal complexes, we have in the past made extensive use of the kinetic and thermodynamic stability of the facially coordinating macrocycle 1,4,7-trimethyl-1,4,7-triazacyclononane (L), which functions as an effective blocking ligand for three facial coor-

dination sites in an octahedral complex.[18] When the remaining three sites are occupied by monodentate labile ligands, hydrolysis reactions often lead to oxo- and/or hydroxo-bridged bi- or polynuclear species. Previously, we have used LVCl₃·dmf as a useful starting material,[8] since the chloride ions are quite labile. In order to obtain an even more reactive species, we have synthesized LV(O₃SCF₃)₃, a mononuclear complex containing very labile trifluoromethanesulfonato ligands.[19]

Experimental Section

Methods and Materials. The ligand 1,4,7-trimethyl-1,4,7-triazacyclononane (L; C₉H₂₁N₃)[20] and the complex LVCl₃·dmf (1)[8] (dmf = dimethylformamide) have been prepared as described previously. All other reagents were purchased from commercial sources and used without further purification.

LV(O₃SCF₃)₃ (2). To 1 (2.5 g; 7.5 mmol) was added dropwise within 30 min trifluoromethanesulfonic acid (10 mL) under an argon atmosphere. During this process the reaction vessel was cooled with ice. Hydrochloride gas evolved, and a deep green solution was obtained. Upon addition of argon-scrubbed, dry diethyl ether (50 mL) a green precipitate formed, which was filtered off under an argon atmosphere, washed with dry ether, and dried. The green microcrystalline product is air-sensitive and was stored under argon (yield: 4.95 g, 97%).

Anal. Calcd for C₁₂H₂₁N₃O₉F₉S₃V: C, 21.5; H, 3.2; N, 6.32. Found: C, 21.3; H, 3.4; N, 6.1.

LV(NCS)₃ (3). To an argon-scrubbed solution of sodium thiocyanate (1 g) in water (10 mL) was added 2 (0.40 g; 0.6 mmol). Within 30 min of stirring at room temperature an orange precipitate formed, which was filtered off, washed with ether, and air-dried. The product may be recrystallized from acetonitrile or acetone (yield: 0.19 g, 80%).

IR (KBr disk): ν(NCS) 2000, 1990 cm⁻¹. Anal. Calcd for C₁₂H₂₁N₆S₃V: C, 36.3; H, 5.3; N, 21.2. Found: C, 36.5; H, 5.3; N, 20.9.

LVO(N₃)₂ (4). To a solution of sodium azide (1.0 g) dissolved in water (15 mL) was added 2 (0.40 g; 0.6 mmol) with stirring in the presence of air. After the mixture was stirred for 30 min at room temperature a blue-green precipitate formed, which was filtered off and recrystallized from a minimum amount of an acetone/water mixture (1:1) (yield: 0.16 g, 78%).

IR (KBr disk) ν(N₃) 2010, ν(V=O) 950 cm⁻¹. Anal. Calcd for C₉H₂₁N₉OV: C, 33.2; H, 6.6; N, 39.1. Found: C, 33.5; H, 6.4; N, 38.9.

LVO(NCO)₂ (5). When the filtrate of the reaction solution described for the synthesis of 6 was allowed to stand at room temperature in an

(13) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401.
(14) (a) Marabella, C. P.; Enemark, J. H.; Miller, K. F.; Bruce, A. E.; Pariyadath, N.; Corbin, J. L.; Stiefel, E. I. *Inorg. Chem.* **1983**, *22*, 3456. (b) Matsumoto, K.; Marutani, Y.; Ooi, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2671. (c) Wieghardt, K.; Backes-Dahmann, G.; Herrmann, W.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 899. (d) Burgmayer, S. J.; Stiefel, E. I. *J. Am. Chem. Soc.* **1986**, *108*, 8310.
(15) Schreiber, P.; Wieghardt, K.; Nuber, B.; Weiss, J. *Polyhedron* **1989**, *8*, 1675.
(16) Giacomelli, A.; Floriani, C.; Duarte, A. O.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1982**, *21*, 3310.
(17) Scheidt, W. R. *Inorg. Chem.* **1973**, *12*, 1758.
(18) Chaudhuri, P.; Wieghardt, K. *Prog. Inorg. Chem.* **1987**, *35*, 329.
(19) Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17.
(20) Wieghardt, K.; Chaudhuri, P.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1982**, *21*, 3086.

open vessel for 2–3 days, deep blue crystals of **5** precipitated, which were filtered off, washed with diethyl ether, and air-dried (yield: 0.7 g, 36%).

IR (KBr disk): ν(NCO) 2180 and 2160, ν(V=O) 950 cm^{-1}. Anal. Calcd for $C_{11}H_{21}N_5O_3V$: C, 41.0; H, 6.6; N, 21.7. Found: C, 41.2; H, 6.8; N, 22.0.

[L₂V₂(NCO)₄O]·2H₂O (6). To an argon scrubbed solution of sodium cyanate (1.0 g) dissolved in water (15 mL) was added **2** (0.40 g; 0.6 mmol). Within 30 min of stirring at room temperature the color of the solution changed to purple. Continuous stirring at 20 °C for 12 h yielded a purple precipitate, which was filtered off, washed with ether, and air-dried. The product is soluble in acetone, acetonitrile, and methylene dichloride (yield: 0.17 g, 42%).

IR (KBr disk): ν(NCO) 2080 cm^{-1}. Anal. Calcd for $C_{22}H_{46}N_{10}O_7V_2$: C, 39.7; H, 6.4; N, 21.0; V, 15.3. Found: C, 40.0; H, 6.4; N, 21.0; V, 15.2.

[L₂V₂(acac)₂O]I₂·2H₂O (7). To a solution of NH₄[HCO₃] (1.0 g) and 2,4-pentanedione (10 mL) in water (20 mL) was added **1** (1.0 g; 3 mmol) under an argon atmosphere. This solution was refluxed for 10 min until a clear purple solution was obtained. Upon addition of sodium iodide (2 g) purple crystals of **7** formed within 12 h at 0 °C (yield: 1.2 g, 42%).

IR (KBr disk): ν(CO) 1569 and 1530 cm^{-1}. Anal. Calcd for $C_{28}H_{60}N_6O_7I_2V_2$: C, 35.46; H, 6.38; N, 8.86. Found: C, 35.2; H, 6.3; N, 8.7.

The hexafluorophosphate or tetraphenylborate salts were prepared as described above by addition of NaPF₆ or Na[BPh₄] instead of NaI.

[L₂V₂O(C₆H₅CO₂)₂]I₂·2H₂O (8). To a solution of sodium benzoate (1.0 g) in water (15 mL) was added **1** (0.3 g, 0.9 mmol) under an argon atmosphere. The solution was refluxed 1 h under anaerobic conditions until a clear deep green solution was obtained. Addition of NaI (1.0 g) initiated the precipitation of green microcrystals, which were collected by filtration, washed with diethyl ether, and air-dried. Recrystallization from acetone or acetonitrile produced green crystals (yield: 0.21 g, 17%).

IR (KBr disk): ν_{as}(CO) 1540, ν_s(CO) 1470 cm^{-1}. Anal. Calcd for $C_{32}H_{56}N_6O_7I_2V_2$: C, 38.72; H, 5.89; N, 8.47; V, 10.26. Found: C, 38.6; H, 5.6; N, 8.4; V, 10.4.

[L₂V₂O₅]·14H₂O (9). To a suspension of ammonium vanadate (0.50 g, 4.3 mmol) in an acetonitrile/water mixture (9:1) (20 mL) was added the cyclic amine L (0.73 g; 4.3 mmol). The mixture was refluxed for 2 h, during which time the color changed to yellow. A colorless residue was filtered off and discarded. From the filtrate yellow crystals precipitated within 2–3 days, which were recrystallized from a minimum amount of the above CH₃CN/H₂O mixture. An identical product was obtained by using V₂O₅ (2 mmol) as starting material and otherwise identical reaction conditions (yield: 0.10 g, 16%). The bright yellow transparent crystals contain 14 molecules of water of crystallization, as was established from the X-ray structure determination. These water molecules were readily removed by storing the material in vacuo over P₂O₅. Upon removal of the water molecules the crystals became turbid and they were found to be amorphous.

IR (KBr disk of a dried sample): ν_{as}(V=O) 898, ν_s(V=O) 869, ν(V—O—V) 722 cm^{-1}. Anal. Calcd for $C_{18}H_{42}N_6O_5V_2$: C, 41.2; H, 8.07; N, 16.02; V, 19.43. Found: C, 40.8; H, 8.0; N, 16.2; V, 19.1.

[L₂V₂O₂(OH)₂(μ-O)](ClO₄)₂ (10). To a solution of **9** (0.20 g; 0.4 mmol) in water (5 mL) was added concentrated HClO₄ (2 mL) at room temperature. A bright yellow precipitate formed instantly, which was filtered off and recrystallized from an acetonitrile solution to which a small amount of 1 M HClO₄ was added. Crystals suitable for X-ray crystallography were grown from such a solution (yield: 0.28 g, 97%).

IR (KBr disk): ν(V=O) 962, ν(V—O—V) 739, ν(V—OH) 657 cm^{-1}. Anal. Calcd for $C_{18}H_{44}N_6O_{13}Cl_2V_2$: C, 29.8; H, 6.1; N, 11.6. Found: C, 29.6; H, 5.9; N, 11.3.

The vanadium content was determined by using Hartkamp's spectrophotometric method.[21]

Physical Measurements. Electronic absorption spectra were recorded in the 200–1200-nm range with a Perkin-Elmer Lambda 9 spectrophotometer, while infrared spectra were recorded with a Perkin-Elmer Model 1702 spectrometer. Solid-state magnetic susceptibilities of powdered samples were measured in the 98–300 K range by using the Faraday method. The apparatus used has been described previously.[8] The magnetic susceptibilities of [L₂V₂(μ-O)(μ-CH₃CO₂)₂]I₂·2H₂O and **7** were measured as a function of temperature in the range 10–300 K. Pascal's constants were used to calculate the diamagnetic corrections. The equipment used for electrochemical measurements has been described elsewhere.[8] Cyclic voltammograms were recorded at scan rates from 20 to 200 mV s^{-1}; the concentration of the electroactive component was ≈10^{-3} M; [n-Bu₄N]PF₆ (0.1 M) was used as the supporting electrolyte. The potentials were referenced versus the ferrocenium/ferrocene couple

(21) Hartkamp, H. *Z. Anal. Chem.* **1961**, *182*, 259.

Table I. Crystallographic Data for Complexes **7**, **9**, and **10**

	7	9	10
chem formula	$C_{28}H_{60}N_6O_7I_2V_2$	[$C_{18}H_{42}N_6O_5V_2$]·14H₂O	$C_{18}H_{44}N_6O_{13}Cl_2V_2$
fw	948.5	776.7	725.4
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
T, °C	22	20	22
a, Å	9.078 (6)	10.587 (3)	8.762 (3)
b, Å	12.785 (8)	8.608 (2)	13.975 (5)
c, Å	16.96 (1)	23.049 (4)	11.988 (3)
β, deg	99.93 (5)	115.74 (2)	101.23 (3)
V, Å³	1939 (6)	1892 (2)	1440 (3)
Z	2	2	2
radiation	Mo Kα (graphite monochromated), λ = 0.710 73 Å		
ρ_{calcd}, g cm^{-3}	1.62	1.36	1.67
μ, cm^{-1}	20.88	5.49	8.84
transm coeff	0.78–1.00	0.76–0.83	0.85–0.98
R^a	0.036	0.052	0.044
R_w^b	0.028	0.051	0.039
goodness of fit	2.51	2.81	2.28

$^a R = \sum \|F_o| - |F_c\|/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table II. Atom Coordinates ($\times 10^4$) and Temperature Factors (Å² $\times$ 10³) for **7**

atom	x	y	z	U^a
I(1)	2231 (1)	5640 (1)	6351 (1)	49 (1)
V(1)	8999 (1)	3804 (1)	9701 (1)	23 (1)
O(1)	10000	5000	10000	23 (1)
N(1)	7858 (3)	2217 (3)	9490 (2)	32 (1)
N(2)	10373 (3)	2849 (2)	10601 (2)	31 (1)
N(3)	7577 (3)	3792 (3)	10614 (2)	32 (1)
C(1)	9110 (4)	1462 (3)	9715 (2)	44 (2)
C(2)	9986 (5)	1703 (3)	10527 (3)	45 (2)
C(3)	10062 (4)	3284 (4)	11366 (2)	47 (2)
C(4)	8426 (4)	3344 (4)	11381 (2)	47 (2)
C(5)	6251 (4)	3138 (3)	10287 (3)	40 (2)
C(6)	6715 (4)	2088 (3)	10013 (3)	41 (2)
C(7)	7166 (5)	1999 (4)	8652 (2)	48 (2)
C(8)	11986 (4)	2985 (3)	10567 (3)	44 (2)
C(9)	7029 (5)	4870 (3)	10749 (3)	47 (2)
O(2)	7385 (3)	4408 (2)	8881 (1)	33 (1)
O(3)	10085 (3)	3420 (2)	8818 (1)	31 (1)
C(11)	6008 (5)	5026 (4)	7667 (3)	64 (2)
C(12)	7369 (4)	4510 (3)	8125 (2)	35 (2)
C(13)	8467 (5)	4154 (3)	7723 (2)	40 (2)
C(14)	9743 (5)	3618 (3)	8071 (2)	33 (2)
C(15)	10796 (5)	3226 (4)	7556 (3)	53 (2)
O_w(1a)	3778 (4)	681 (3)	763 (2)	64 (1)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

as internal standard, which may be converted to normal hydrogen electrode (NHE) potentials by assuming the former potential to be 0.40 V vs NHE[22] in acetonitrile solutions.

X-ray Crystallography. Intensities and lattice parameters of a purple column-shaped crystal of **7**, a yellow prismatic crystal of **9**, and a tabular-shaped yellow crystal of **10** were measured on AED II (Siemens) (**7** and **10**) and CAD 4 (Enraf-Nonius) (**9**) diffractometers at room temperature. Crystal parameters and additional details of the data collection and refinement are given in Table I. Empirical absorption corrections (ψ scans) were carried out in each case (7 reflections in the range 9 < 2θ < 46°). All structures were solved by conventional Patterson and difference Fourier methods and refined[23] with anisotropic thermal parameters for all non-hydrogen atoms. Neutral-atom scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from ref 24. All methylene hydrogen atoms were placed at calculated positions with d(C—H) = 1.08 Å) and group isotropic temperature factors, while the methyl groups were treated as rigid bodies, each with three rotational variables. The function minimized during full-matrix least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(I)$ for **7** and **10** and $w = [\sigma^2(F_o + 0.00005F_o)^2]^{-1}$ for **9**. The positions of the hydrogen

(22) Koepp, H. M.; Wendt, H.; Strehlow, H. *Z. Elektrochem.* **1960**, *64*, 483.
(23) Full-matrix least-squares refinement was performed with the SHELX-76 system: Sheldrick, G. M. "SHELX-76" University of Cambridge, Cambridge, England, 1976.
(24) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 99, 149.

Table III. Atom Coordinates ($\times 10^4$) and Temperature Factors ($\text{Å}^2 \times 10^3$) for 9

atom	x	y	z	U
V(1)	0.5214 (1)	0.1454 (1)	0.4484 (1)	23 (1)
O(1)	0.5000	0.0000	0.5000	23 (2)
O(2)	0.4599 (3)	0.3052 (3)	0.4656 (1)	32 (1)
O(3)	0.6925 (3)	0.1746 (3)	0.4800 (1)	34 (1)
N(1)	0.5066 (4)	0.2599 (4)	0.3575 (2)	38 (2)
N(2)	0.5432 (4)	-0.0570 (4)	0.3854 (2)	35 (2)
N(3)	0.2965 (4)	0.0907 (4)	0.3711 (2)	31 (2)
C(1)	0.5808 (8)	0.1690 (6)	0.3282 (4)	86 (5)
C(2)	0.5814 (9)	-0.0018 (7)	0.3352 (4)	111 (6)
C(3)	0.4134 (4)	-0.1472 (7)	0.3566 (4)	107 (4)
C(4)	0.2813 (5)	-0.0615 (6)	0.3406 (4)	80 (4)
C(5)	0.2519 (5)	0.2132 (8)	0.3218 (3)	82 (4)
C(6)	0.3632 (4)	0.2845 (10)	0.3083 (3)	104 (5)
C(11)	0.5782 (6)	0.4121 (6)	0.3746 (3)	51 (3)
C(21)	0.6536 (5)	-0.1656 (6)	0.4271 (2)	41 (2)
C(31)	0.2000 (5)	0.0962 (6)	0.4013 (2)	41 (2)
O$_w$(1)	0.7362 (3)	0.4680 (4)	0.5479 (2)	44 (2)
O$_w$(2)	1.0344 (4)	0.3979 (4)	0.4640 (2)	58 (2)
O$_w$(3)	0.8311 (4)	0.4003 (4)	0.7665 (2)	60 (2)
O$_w$(4)	1.1036 (4)	0.1676 (5)	0.6577 (2)	62 (2)
O$_w$(5)	0.9346 (4)	0.4034 (4)	0.6747 (2)	54 (2)
O$_w$(6)	0.8680 (4)	0.3835 (5)	0.3278 (2)	71 (2)
O$_w$(7)	1.0249 (3)	-0.1414 (4)	0.4802 (2)	46 (2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table IV. Atom Coordinates ($\times 10^4$) and Temperature Factors ($\text{Å}^2 \times 10^3$) for 10

atom	x	y	z	U^a
V(1)	1595 (1)	5815 (1)	4980 (1)	22 (1)
O(1)	0	5000	5000	24 (1)
O(2)	2979 (3)	5119 (2)	4768 (2)	35 (1)
O(3)	959 (4)	6395 (2)	3646 (2)	34 (1)
N(1)	3428 (4)	6950 (2)	5437 (3)	27 (1)
N(2)	286 (4)	7071 (2)	5668 (4)	25 (1)
N(3)	2266 (4)	5693 (2)	6860 (2)	26 (1)
C(1)	2800 (5)	7895 (3)	5742 (4)	31 (1)
C(2)	1074 (5)	7949 (3)	5336 (4)	32 (1)
C(3)	408 (5)	7005 (3)	6919 (3)	36 (2)
C(4)	899 (5)	6023 (3)	7340 (3)	37 (2)
C(5)	3722 (5)	6256 (3)	7339 (3)	37 (2)
C(6)	4567 (5)	6547 (3)	6424 (4)	36 (2)
C(7)	4231 (6)	7102 (3)	4480 (4)	46 (2)
C(8)	-1379 (5)	7079 (3)	5113 (4)	39 (2)
C(9)	2561 (6)	4660 (3)	7170 (4)	43 (2)
Cl(1)	2552 (1)	10308 (1)	3714 (1)	37 (1)
O(11)	2752 (5)	9367 (3)	3334 (3)	74 (2)
O(12)	2102 (7)	10316 (3)	4741 (3)	124 (3)
O(13)	1418 (6)	10763 (4)	2922 (4)	125 (3)
O(14)	3918 (6)	10810 (4)	3733 (5)	154 (3)
H(3)	1413	6246	3031	80

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor, except for C(6) and H(3).

atoms of water molecules of crystallization in crystals of **7** were located in the final difference Fourier map and were readily refined. Only five of the fourteen water hydrogen atoms could be located unequivocally from difference syntheses in crystals of **9**, as a result of their participation in O–H···O hydrogen bonding. They were included in the refinement at fixed positions with a group isotropic temperature factor. The hydrogen atom at the V–OH group in crystals of **10** was also located and included in a fixed position in the final refinement cycle. Atom coordinates for **7**, **9**, and **10** are given in Tables II–IV, respectively. Positional parameters for hydrogen atoms are available in the supplementary material.

Results and Discussion

Syntheses. Recently, we have described a high-yield synthesis for the mononuclear vanadium(III) complex LVCl$_3$·dmf (**1**) from VCl$_3$ dissolved in dimethylformamide (dmf) and the tridentate macrocycle 1,4,7-trimethyl-1,4,7-triazacyclononane (L).[8] It was found that the chloride ligands are relatively labile and **1** is an excellent starting material for the synthesis of binuclear vanadium(III) complexes. Thus, hydrolysis of **1** in an aqueous solution of sodium acetate under anaerobic conditions yields the green binuclear [L$_2$V$_2$(μ-O)(μ-O$_2$CCH$_3$)$_2$]$^{2+}$ species, which contains the (μ-oxo)bis(μ-acetato)divanadium(III) core. When sodium benzoate was used instead of sodium acetate and sodium iodide was added, green microcrystals of **8** containing the (μ-oxo)bis(μ-benzoato)divanadium(III) core precipitated. Alkaline hydrolysis of **1** in the presence of acetylacetone under anaerobic conditions afforded purple crystals of **7** upon addition of NaI, which is a rare species containing the linear [V–O–V]$^{4+}$ moiety.

In order to obtain an even more reactive mononuclear L^{III}X$_3$ complex, **1** was treated with trifluoromethanesulfonic acid in the absence of oxygen. Gaseous hydrogen chloride evolved immediately, and a clear green solution formed, from which a green precipitate of **2** was obtained upon addition of diethyl ether. **2** is moisture- and air-sensitive and was kept under a dry argon atmosphere. In the infrared spectrum a strong peak at 1350 cm^{-1} (ν_a(SO$_3$)) is indicative of O-coordinated trifluoromethanesulfonato ligands.[19] The temperature-independent magnetic moment of 2.62 μ_B (98–300 K) is in agreement with the spin-only value of 2.73 μ_B for octahedral vanadium(III) (d^2) complexes.

The CF$_3$SO$_3^-$ ligands in **2** are good leaving groups and, consequently, are readily displaced by stronger nucleophiles. Thus, from an aqueous solution of **2** and NaSCN, orange crystals of **3** precipitated under anaerobic conditions. **3** has a temperature-independent (98–293 K) magnetic moment of 2.67 μ_B.

When the above substitution reaction of **2** was carried out in the presence of oxygen, vanadyl complexes of the type LVOX$_2$

formed (X = N$_3^-$ (**4**), NCO$^-$ (**5**)). **4** and **5** exhibit a strong ν(V=O) band in the infrared spectrum at 950 cm^{-1}, respectively. Both have temperature-independent magnetic moments of 1.72 μ_B, respectively, which is typical for monomeric octahedral vanadium(IV) complexes.

Interestingly, hydrolysis of **2** in the absence of oxygen in an aqueous solution of NaOCN affords the purple precipitate **6** within 12 h at room temperature. **6** is a neutral binuclear vanadium(III) complex containing again a [V–O–V]$^{4+}$ core. The magnetic properties of **6** are described below.

Finally, we have synthesized two novel complexes of vanadium(V) that contain the coordinated tridentate macrocycle L. The reaction of L with NH$_4$VO$_3$ or, alternatively, V$_2$O$_5$ in an acetonitrile/water mixture (9:1) affords a deep yellow solution from which bright yellow crystals of [L$_2$V$_2$O$_5$]·14H$_2$O (**9**) precipitated within 2–3 days. These translucent crystals became turbid when dried. Upon storage of the crystals in vacuo over P$_2$O$_5$ for 2 days, the water molecules of crystallization could be completely removed. **9** is diamagnetic; in the infrared spectrum the ν_{as}(V=O) and ν_s(V=O) stretching frequencies of a cis-dioxovanadium(V) moiety have been observed at 898 and 869 cm^{-1}, respectively. In addition, a ν_{as}(V—O—V) band at 722 cm^{-1} has been detected. These data suggest the presence of the hitherto unknown [O$_2$V—O—VO$_2$] structural unit in **9**.

The cis-VO$_2$ moieties in **9** are readily protonated in acidic aqueous solution, forming the cis-VO(OH) unit. Acidification of an aqueous solution of **9** with a few drops of concentrated HClO$_4$ initiates the precipitation of yellow **10**. The infrared spectrum of **10** exhibits one ν(V=O) band at 962 cm^{-1}, the ν_a(V—O—V) band is observed at 739 cm^{-1}, and an additional, new peak at 657 cm^{-1} is assigned to the V—OH stretching frequency; two weak bands at 3620 and 3580 cm^{-1} are due to ν-(O—H) stretching frequencies.

Floriani and co-workers[16] have drawn attention to the functional similarity between the cis-VO$_2$ group and an organic carboxylate group. Thus, [O$_2$V(Q)$_2$]$^-$, where Q represents the 8-quinolinato anion used frequently in analytical chemistry, is protonated in acidic solution, producing the acid [O(OH)V(Q)$_2$] (pK_a 6.3).[16,25] The latter species has not been characterized by X-ray crystallography, and therefore, the protonation site has been a matter of some discussion, but protonation at one of the oxygen atoms of the cis-VO$_2$ group appears to be most likely in the light of Scheidt's structure of (Q)$_2$V(O)(O-i-Pr),[17] which is the inorganic

(25) Riechel, T. L.; Sawyer, D. T. *Inorg. Chem.* **1975**, *14*, 1869.
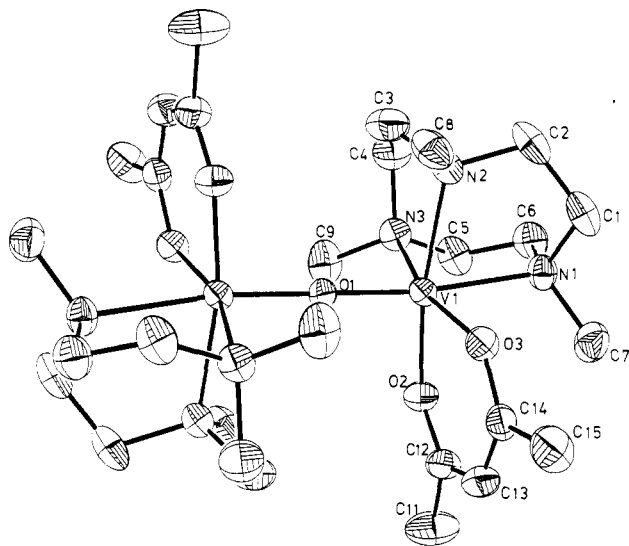
Figure 1. Structure of the dication $[L_2V_2(acac)_2(\mu\text{-}O)]^{2+}$ in crystals of **7**.

Figure 2. Structure of the neutral complex molecule in crystals of **9**.

Table V. Selected Bond Distances (Å) and Angles (deg) for **7**

V(1)–O(1)	1.806 (1)	V(1)–N(1)	2.277 (3)
V(1)–N(2)	2.173 (3)	V(1)–N(3)	2.181 (3)
V(1)–O(2)	1.994 (2)	V(1)–O(3)	1.990 (3)
N(1)–C(6)	1.486 (6)	N(1)–C(1)	1.490 (5)
N(2)–C(2)	1.506 (5)	N(1)–C(7)	1.478 (5)
N(2)–C(8)	1.486 (5)	N(2)–C(3)	1.483 (5)
N(3)–C(5)	1.492 (5)	N(3)–C(4)	1.506 (5)
C(1)C(2)	1.499 (5)	N(3)–C(9)	1.495 (5)
C(5)–C(6)	1.504 (6)	C(3)–C(4)	1.492 (6)
O(3)–C(14)	1.278 (4)	O(2)–C(12)	1.286 (5)
C(12)–C(13)	1.379 (6)	C(11)–C(12)	1.495 (6)
C(14)–C(15)	1.488 (6)	C(13)–C(14)	1.387 (6)
O(1)–V(1)–N(1)	172.4 (1)	O(1)–V(1)–N(2)	94.5 (1)
N(1)–V(1)–N(2)	78.5 (1)	O(1)–V(1)–N(3)	97.9 (1)
N(1)–V(1)–N(3)	78.3 (1)	N(2)–V(1)–N(3)	80.5 (1)
O(1)–V(1)–O(2)	98.1 (1)	N(1)–V(1)–O(2)	88.6 (1)
N(1)–V(1)–O(2)	166.3 (1)	N(3)–V(1)–O(2)	92.5 (1)
O(1)–V(1)–O(3)	97.5 (1)	N(1)–V(1)–O(3)	86.2 (1)
N(2)–V(1)–O(3)	95.2 (1)	N(3)–V(1)–O(3)	164.4 (1)
O(2)–V(1)–O(3)	88.3 (1)	V(1)–O(1)–V(1a)	180.0
V(1)–O(2)–C(12)	128.0 (2)	V(1)–O(3)–C(14)	129.0 (3)
O(2)–C(12)–C(11)	115.4 (4)	O(2)–C(12)–C(13)	125.1 (3)
C(11)–C(12)–C(13)	119.5 (4)	C(12)–C(13)–C(14)	125.1 (4)
O(3)–C(14)–C(13)	124.2 (4)	O(3)–C(14)–C(15)	116.4 (3)
C(13)–C(14)–C(15)	119.4 (3)		

Table VI. Selected Bond Distances (Å) and Angles (deg) for **9**

O(1)–V(1)	1.807 (1)	O(2)–V(1)	1.642 (3)
O(3)–V(1)	1.653 (3)	N(1)–V(1)	2.259 (4)
N(2)–V(1)	2.343 (4)	N(3)–V(1)	2.319 (3)
C(1)–N(1)	1.465 (4)	C(6)–N(1)	1.463 (4)
C(11)–N(1)	1.479 (6)	C(2)–N(2)	1.461 (4)
C(3)–N(2)	1.463 (4)	C(21)–N(2)	1.479 (6)
C(4)–N(3)	1.461 (4)	C(5)–N(3)	1.469 (4)
C(31)–N(3)	1.468 (5)	C(2)–C(1)	1.478 (3)
C(4)–C(3)	1.480 (3)	C(6)–C(5)	1.477 (3)
O(2)–V(1)–O(1)	104.2 (1)	O(3)–V(1)–O(1)	104.0 (1)
O(3)–V(1)–O(2)	103.9 (2)	N(1)–V(1)–O(1)	159.2 (1)
N(1)–V(1)–O(2)	89.0 (1)	N(1)–V(1)–O(3)	87.9 (1)
N(2)–V(1)–O(1)	88.1 (1)	N(2)–V(1)–O(2)	158.2 (1)
N(2)–V(1)–O(3)	90.1 (1)	N(2)–V(1)–N(1)	74.6 (1)
N(3)–V(1)–O(1)	89.2 (1)	N(3)–V(1)–O(2)	88.5 (1)
N(3)–V(1)–O(3)	158.8 (1)	N(3)–V(1)–N(1)	75.0 (1)
N(3)–V(1)–N(2)	73.6 (1)	V(1)–O(1)–V(1)	180.0

$[(tacn)_2Fe_2(acac)_2(\mu\text{-}O)](ClO_4)_2$,[26] where tacn represents the tridentate ligand 1,4,7-triazacyclononane, this trans influence has also been observed albeit to a lesser extent ($\Delta(Fe\text{-}N_{trans} - Fe\text{-}N_{cis})$ = 0.066 Å). Note that in the latter complex the $[Fe\text{-}O\text{-}Fe]^{4+}$ unit is not linear (Fe–O–Fe = 158.6 (3)°). In $[(THF)_6Cl_4V_2\text{-}(\mu\text{-}O)]$ the structural trans influence of the μ-oxo group is also clearly observed ($\Delta(V\text{-}O_{THF,trans} - V\text{-}O_{THF,cis})$ = 0.08 Å).[6] In Christou's complex the vanadium(III) centers are five-coordinate (trigonal bipyramidal) and the position trans to the oxo group is vacant.[7]

The coordination geometry and dimensions of the acac ligand in **7** are very similar to those in $V(acac)_3$;[27] the six-membered chelate ring is planar within experimental uncertainty. The three five-membered chelate rings V–N–C–C–N of each coordinated macrocyclic triamine have λλλ and δδδ conformations at both of the two V(III) centers within one binuclear cation (meso form). The coordinated macrocycle is not disordered in crystals of **7**, and consequently, the C–C and C–N bond distances are in the expected range for such single bonds (≈1.50 Å). Due to the steric constraints of the nine-membered macrocycle the N–V–N bond angles deviate significantly from the ideal octahedral angle of 90° (Table V).

In crystals of **7** the water molecule of crystallization is weakly hydrogen bonded to the iodide anions (I···H–O_w contacts are at 3.546 (6) and 3.549 (6) Å).

Crystals of **9** consist of the neutral binuclear complex $[L_2V_2O_4(\mu\text{-}O)]$ and water molecules of crystallization. Figure 2 displays the structure of the complex molecule; selected bond distances and angles are given in Table VI. The neutral molecule comprises the $[O_2V\text{-}O\text{-}VO_2]^0$ core, which has to the best of our knowledge not been crystallographically characterized previously. This unit has two terminal oxygen atoms in cis position with respect to each other at each vanadium(V) center. The average terminal V–O distance of 1.648 Å is quite short and indicates double-bond character and agrees well with V=O distances in

analogue of an organic ester. **10** represents the first structurally characterized example of such an inorganic acid with a VO(OH) functional group (see below).

Description of Structures. Crystals of **7** consists of the binuclear dication $[L_2V_2(acac)_2(\mu\text{-}O)]^{2+}$, uncoordinated iodide anions, and water molecules of crystallization. Figure 1 shows the structure of the complex in **7**; selected bond distances and angles are summarized in Table V. Two vanadium(III) ions are bridged by a linear μ-oxo group; the cation possesses crystallographically required symmetry C_i. Each V(III) ion is in pseudooctahedral environment comprising a facially coordinated macrocycle L, a bidentate acac ligand, and an oxygen atom of the oxo bridge (VN_3O_3 coordination sphere). The $V\text{-}O_{oxo}$ bond distance of 1.806 (1) Å agrees well with those determined for the other two crystallographically characterized complexes containing the linear $[V\text{-}O\text{-}V]^{4+}$ unit, namely $[(THF)_3Cl_2VOVCl_2(THF)_3]$ with 1.769 (5) Å[6] and $[V_2O(SCH_2CH_2NMe_2)_4]$ with 1.803 (4) and 1.822 (4) Å.[7] The $V\text{-}O_{oxo}$ bond lengths are rather short and indicate considerable double-bond character. The V–N bond distance in the trans position with respect to the oxo bridge is significantly longer than the two $V\text{-}N_{cis}$ distances ($\Delta(V\text{-}N_{trans} - $ average $V\text{-}N_{cis})$ = 0.10 Å). This indicates a pronounced structural trans influence of the oxo group. In the corresponding binuclear iron(III) complex
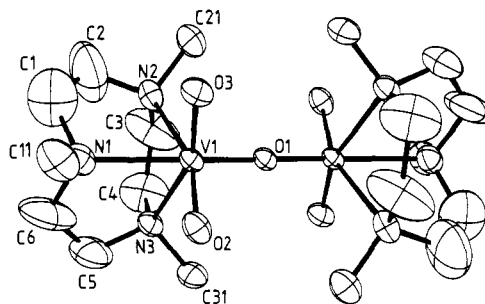
(26) Wieghardt, K.; Pohl, K.; Bossek, U.; Nuber, B.; Weiss, J. *Z. Naturforsch.* **1988**, *43B*, 1184.

(27) Morosin, B.; Montgomery, H. *Acta Crystallogr., Sect. B* **1969**, *25*, 1354.

Table VII. Hydrogen Bonds in the Crystal Lattice of
$[C_{18}H_{42}N_6O_5V_2]\cdot14H_2O$ (9)

bond	length, Å^a	sym position of second O atom
$O_w(1)\cdots O(2)$	2.767	$1 - x, 1 - y, 1 - z$
$O_w(1)\cdots O_w(2)$	2.808	$2 - x, 1 - y, 1 - z$
$O_w(1)\cdots O_w(5)$	2.816	x, y, z
$O_w(2)\cdots O_w(2)$	2.726	$2 - x, 1 - y, 1 - z$
$O_w(2)\cdots O_w(7)$	2.762	$2 - x, -y, 1 - z$
$O_w(3)\cdots O_w(4)$	2.789	$2 - x, {}^1/_2 + y, {}^3/_2 - z$
$O_w(3)\cdots O_w(5)$	2.773	x, y, z
$O_w(3)\cdots O_w(6)$	2.764	$x, {}^1/_2 - y, {}^1/_2 + z$
$O_w(5)\cdots O_w(6)$	2.801	$2 - x, 1 - y, 1 - z$
$O_w(7)\cdots O(3)$	2.737	$2 - x, -y, 1 - z$
$O_w(7)\cdots O_w(7)$	2.730	$2 - x, -y, 1 - z$

^{a} The estimated standard deviation for all $O\cdots O$ contacts is 0.006 Å.
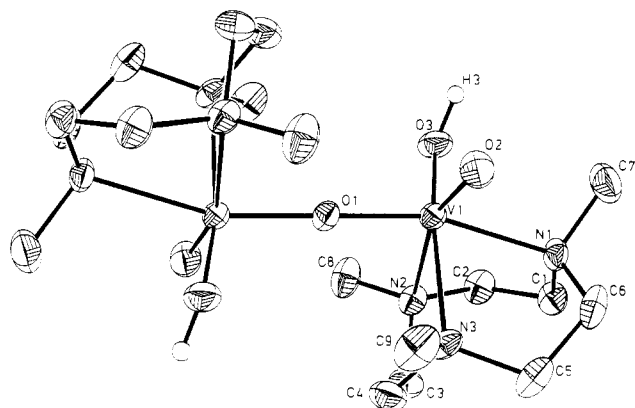
Figure 3. Structure of the dication $[L_2V_2O_2(OH)_2(\mu\text{-}O)]^{2+}$ in crystals of **10**.

monomeric octahedral complexes containing a *cis*-dioxo-vanadium(V) unit.[28] The bond angle of the *cis*-VO₂ unit is 103.9 (2)°. The V–O_{oxo} distance is 1.807 (1) Å, which is nearly identical with the corresponding distance in complexes containing the [V–O–V]⁴⁺ unit despite the fact that the ionic radii of V(V) and V(III) in an octahedral environment differ by –0.10 Å. The V–O–V unit in **9** is again linear; the molecules in **9** possess crystallographically imposed C_i symmetry. The two terminal oxo groups exert a strong structural trans influence on the V–N distances in trans positions with respect to these bonds. Thus, the average V–N_{trans} distance of 2.331 is longer by 0.072 Å than the V–N(1) distance, which is trans with respect to the longer V–O_{oxo} bond.

The methylene carbon atoms of the cyclic triamine exhibit large anisotropic thermal parameters that are physically meaningless; they reflect a disorder of the λλλ or δδδ conformation of the V–N–C–C–N chelate rings. Attempts to model this disorder by a split-atom model failed. This effect has been observed in many crystal structures of binuclear complexes containing coordinated cyclic triamine ligands.[29]

9 contains 14 molecules of water of crystallization/binuclear vanadium(V) molecule. These water molecules form a series of short O–H···O contacts, which are summarized in Table VII. Of interest is the observation that both terminal oxo ligands of the

Table VIII. Selected Bond Distances (Å) and Angles (deg) for **10**

|			
$V(1)-O(1)$	1.807 (1)	$V(1)-O(2)$	1.612 (3)
$V(1)-O(3)$	1.783 (3)	$V(1)-N(1)$	2.247 (3)
$V(1)-N(2)$	2.333 (3)	$V(1)-N(3)$	2.222 (3)
$O(1)-V(1a)$	1.807 (1)	$O(3)-H(3)$	0.927 (3)
$N(1)-C(1)$	1.503 (5)	$N(1)-C(6)$	1.501 (5)
$N(1)-C(7)$	1.474 (6)	$N(2)-C(2)$	1.499 (5)
$N(2)-C(3)$	1.485 (5)	$N(2)-C(8)$	1.481 (5)
$N(3)-C(4)$	1.499 (6)	$N(3)-C(5)$	1.513 (5)
$N(3)-C(9)$	1.501 (5)	$C(1)-C(2)$	1.498 (6)
$C(3)-C(4)$	1.496 (6)	$C(5)-C(6)$	1.494 (6)
$O(1)-V(1)-O(2)$	103.3 (1)	$O(1)-V(1)-O(3)$	101.0 (1)
$O(2)-V(1)-O(3)$	104.3 (1)	$O(1)-V(1)-N(1)$	163.6 (1)
$O(2)-V(1)-N(1)$	86.6 (1)	$O(3)-V(1)-N(1)$	88.9 (1)
$O(1)-V(1)-N(2)$	92.0 (1)	$O(2)-V(1)-N(2)$	161.1 (1)
$O(3)-V(1)-N(2)$	83.4 (1)	$N(1)-V(1)-N(2)$	76.1 (1)
$O(1)-V(1)-N(3)$	89.5 (1)	$O(2)-V(1)-N(3)$	93.2 (1)
$O(3)-V(1)-N(3)$	156.8 (1)	$N(1)-V(1)-N(3)$	76.8 (1)
$N(2)-V(1)-N(3)$	75.5 (1)	$V(1)-O(1)-V(1a)$	180.0
$V(1)-O(3)-H(3)$	120.2 (2)		

cis-VO₂ moiety (O(2) and O(3)) form strong hydrogen bonds to water molecules $O_w(1)$ and $O_w(7)$ at 2.767 (6) and 2.737 (6) Å, respectively. This indicates that these terminal oxo groups are quite basic.

Crystals of **10** consist of the dication $[L_2V_2O_2(OH)_2(\mu\text{-}O)]^{2+}$ and uncoordinated perchlorate anions; the dication possesses crystallographically required symmetry C_i. Figure 3 shows the structure of the complex and the atom-labeling scheme; selected bond distances and angles are summarized in Table VIII. The overall structure of the binuclear complex in **10** is quite similar to the structure of the neutral complex in **9** with the remarkable difference that one terminal oxo ligand at each vanadium(V) center is protonated (O(3)). This proton has been identified in the final difference Fourier map and has been included in a fixed position in the final refinement cycles. The O(3)–H(3) distance at 0.927 (3) Å is chemically reasonable as is the bond angle V–O–H of 120.2 (2)°. Consequently, the distance V(1)–O(3) at 1.783 (3) Å is longer than the distance V(1)–O(2) at 1.612 (3) Å, which corresponds to a normal V=O bond length. The V–O_{oxo} bond distance of 1.807 (1) Å is identical with the corresponding bond in **9**. The [V–O–V]⁸⁺ unit is again linear. The three V–N distances are not equivalent; the longest distance at 2.333 (3) Å (V(1)–N(2)) is in position trans to the shortest V–O distance (V(1)–O(2)) whereas the shortest V–N bond length of 2.222 (3) Å (V(1)–N(3)) is in a trans position with respect to the V–OH group.

In contrast to the structure of **9** the tridentate amine ligands are not disordered in **10**. The anisotropic thermal parameters of the methylene carbon atoms are normal, and the C–C and C–N bond distances are in the usual range for such single bonds (Table VIII). The perchlorate oxygen atom O(14) is weakly hydrogen bonded to the V–OH group (O(3)···O(14) = 2.990 (6) Å; H-(3)···O(14) = 2.165 Å).

Magnetic Properties of [V–O–V]⁴⁺ Complexes. The magnetic properties of complexes containing the [V–O–V]⁴⁺ structural unit are not well understood, which is mainly due to the limited number of structurally characterized species. Low-temperature magnetic susceptibility data have not been reported to date. For [(TH-F)₃Cl₂VOVCl₂(THF)₃] no magnetic measurements have been reported, but for [V₂O(SCH₂CH₂NMe₂)₄] an effective magnetic moment of 2.83 μ_B/V has been determined at 23 °C by using Evans' NMR method and solid-state measurements. This value would indicate the absence of an appreciable coupling between the two vanadium(III) centers. We have previously reported an intramolecular ferromagnetic exchange coupling in both [L₂V₂-(μ-O)(μ-O₂CCH₃)₂]I₂·2H₂O and in [{HB(pz)₃}₂V₂(μ-O)(μ-O₂CCH₃)₂] that was derived from magnetic susceptibility measurements in the temperature range 98–293 K on solid samples by using the Faraday method.[8] Both complexes contain the (μ-oxo)bis(μ-carboxylato)divanadium(III) core with a V···V distance of ≈3.25 Å, a V–O_{oxo} bond length of 1.794 (4) Å, and a V–O–V bond angle of 130.2°.

(28) See for example: (a) Jeannin, Y.; Launay, J. P.; Sedjadi, M. A. S. *J. Coord. Chem.* **1981**, *11*, 27. (b) Scheidt, W. R.; Tsai, C.; Hoard, J. L. *J. Am. Chem. Soc.* **1971**, *93*, 3867. (c) Scheidt, W. R.; Countryman, R.; Hoard, J. L. *J. Am. Chem. Soc.* **1971**, *93*, 3878. (d) Kojima, A.; Okazaki, K.; Ooi, S.; Saito, K. *Inorg. Chem.* **1983**, *22*, 1168. (e) Neves, A.; Walz, W.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1988**, *27*, 2484.

(29) Hartman, J. R.; Rardin, R. L.; Chaudhuri, P.; Pohl, K.; Wieghardt, K.; Nuber, B.; Weiss, J.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 7387.

(30) Li, X.; Lah, M. S.; Pecoraro, U. L. *Inorg. Chem.* **1988**, *27*, 4657.

(31) McCarthy, P. J.; Güdel, H. U. *Coord. Chem. Rev.* **1988**, *88*, 69.

(32) Neubold, P.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1989**, *28*, 459.
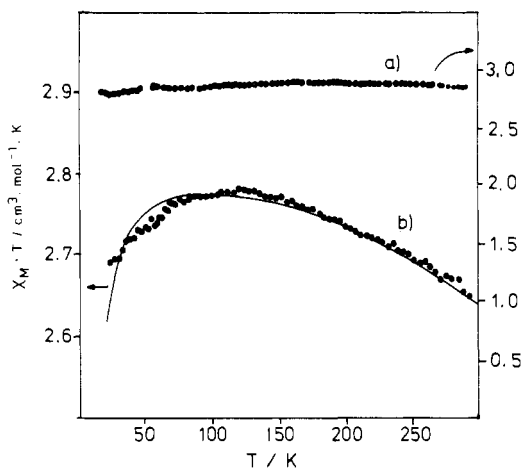
Figure 4. Plot of $\chi_M T$ vs T for solid samples of (a) $[L_2V_2(\mu\text{-O})(\mu\text{-}O_2CCH_3)_2]I_2\cdot2H_2O$ and (b) **7**. Note the different scales for $\chi_M T$ of both compounds. The solid line represents the data best fit to the isotropic Heisenberg model for spin-exchange coupling (see text).

We have now extended these measurements to lower temperatures for $[L_2V_2(\mu\text{-O})(\mu\text{-}O_2CCH_3)_2]I_2\cdot2H_2O$. Figure 4 shows a plot of $\chi_M T$ vs T that indicates nearly ideal Curie behavior; the value of $\chi_M T$ of 2.88 ± 0.03 cm^3 mol^{-1} K is within experimental error independent of the temperature. It corresponds to a temperature-independent magnetic moment of 4.82 μ_B/binuclear complex (or 3.41 μ_B/V), which is significantly larger than the spin-only value of 2.83 μ_B for an octahedral vanadium(III) complex. In contrast, the product $\chi_M T$ for the binuclear complex **7** containing a linear $[V\text{-O}\text{-}V]^{4+}$ core increases with decreasing temperature in the range $298\text{-}\approx110$ K where it reaches a maximum and decreases then with decreasing temperature in the range 100-30 K. The overall effect is small; the maximum value of $\chi_M T$ is 2.79 cm^3 mol^{-1} K at 120 K, and the minimal value is 2.69 cm^3 mol^{-1} K at 30 K. The magnetic moment per vanadium(III) ion varies thus between 3.35 and 3.29 μ_B, which is again significantly larger than the spin-only value and may indicate an intramolecular ferromagnetic exchange coupling between the two vanadium(III) centers ($S = 2$ ground state). The observed decrease of $\chi_M T$ at temperatures below 90 K may be due to either zero-field splitting or an intermolecular antiferromagnetic coupling between binuclear complexes in the solid state. A reasonable fit to the data was obtained by using the Hamiltonian $H = -J\hat{S}_1\cdot\hat{S}_2$ with $J = +224$ cm^{-1} and $g = 1.93$ ($S_1 = S_2 = 1$) and assuming zero-field splitting to be operative. A splitting parameter D_c of $+18$ cm^{-1} was calculated. This latter value should not be taken too seriously; it may be artificial due to the above-mentioned possibility of an intermolecular antiferromagnetic interaction.

We have not been able to fit the experimental data for $[L_2V_2(\mu\text{-O})(\mu\text{-}O_2CCH_3)_2]I_2\cdot2H_2O$ satisfactorily, but the exchange coupling constant J is estimated to be at least $+400$ cm^{-1}. This value is not in agreement with the previously reported value.[8,33] Thus, an $S = 2$ ground state is also observed for this binuclear species.

Magnetic susceptibility data of a powdered sample of **6** have been measured in the temperature range 100-300 K by using the Faraday method. The product $\chi_M T$ is within experimental uncertainty constant (2.88 cm^3 mol^{-1} K), which corresponds to a magnetic moment of 3.41 μ_B/V, indicating again an intramolecular ferromagnetic exchange coupling of considerable strength ($J \geq +400$ cm^{-1}; $S = 2$ ground state). Very similar behavior has been observed for **8**; $\chi_M T$ is again constant in the temperature range 100-293 K (3.08 cm^3 mol^{-1} K), which corresponds to a magnetic moment of 3.52 μ_B/V ($S = 2$ ground state).

In summary, the available magnetic data on binuclear complexes containing the $[LV\text{-O}\text{-}VL]^{4+}$ structural unit (with bent or linear V-O-V groups) appear to indicate substantial intramolecular ferromagnetic exchange coupling with $S = 2$ ground

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(33) A computational error had occurred in the previously reported J values.

Table IX. Electronic Spectral Data and Magnetic Properties of Complexes

complex	electronic spectral data[a] λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})	magnetism magnetic moment, μ_B[b]
2	570, 410 (sh)	2.62
3	434 (7500), 377 (3500), 324 (1.2 × 10^4), 302 (8000)	2.67
4	786 (58), 594 (76)	1.72
5	770 (34), 561 (35)	1.72
6	650 (sh), 513 (5200), 360 (3600), 317 (3200), 274 (6700), 200 (10.6 × 10^3)[d]	3.57 at 98 K,[c] 3.41 at 298 K
7	539 (7800), 393 (1520), 317 (8800), 275 (12.5 × 10^3), 223 (11.1 × 10^3)[d]	3.52[c]
8	708 (1900), 453 (2850), 360 (1900), 329 (2010)[d]	3.53[c]
9	337 (8300), 282 (9900), 231 (9300)	diamagnetic
10	395 (5600), 345 (6500), 280 (sh), 240 (11.7 × 10^3)[d]	diamagnetic

[a] Measured in acetonitrile. [b] Magnetic moments in the temperature range 98-298 K. [c] Magnetic moment per vanadium center. [d] Extinction coefficients are per dimer.
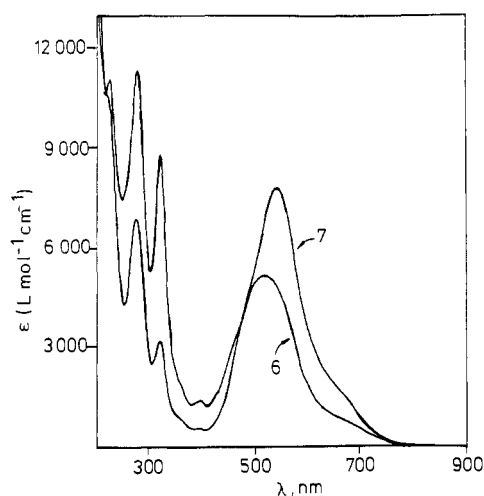
Figure 5. Electronic spectra of **6** and **7** in acetonitrile at 20 °C.

states. Christou's complex may be an exception, since the reported data at room temperature seem to point to uncoupled vanadium(III) ions. A full magnetic study of this and the $[(THF)_3Cl_2V\text{-}O\text{-}VCl_2(THF)_3]$ complex would be very desirable. Note that the mononuclear species $LV(NCS)_3$, $LVCl_3\cdot dmf$, and $LV(O_3SCF_3)_3$ exhibit temperature-independent magnetic moments (98-298 K) in the range 2.6-2.8 μ_B, which are in good agreement with the expected spin-only value of 2.83 μ_B for a d^2 electronic configuration in O_h symmetry.

Electronic Spectra. Electronic spectral data are summarized in Table IX; Figure 5 displays the spectra of the μ-oxo-bridged vanadium(III) complexes **6** and **7**. Since Newton and Baker's kinetic study of V(II) and V(IV) perchlorates in acidic aqueous solution, it has been recognized that compounds containing the linear $[V\text{-O}\text{-}V]^{4+}$ core exhibit an intense absorption maximum in the visible region (400-500 nm). These include $[(THF)_3Cl_2VOVCl_2(THF)_3]$ (487 nm in CH_3CN),[6] $[V_2O(SCH_2CH_2NMe_2)_4]$ (463 nm in CH_3CN),[7] and $V_2O(ttha)^{2-}$ (450 nm at pH 7.5).[9] **6** and **7** display this charge-transfer transition at 497 and 539 nm, respectively.

The spectra of complexes with a $(\mu\text{-oxo})bis(\mu\text{-carboxylato})$-divanadium(III) core are quite different. Two very intense absorptions in the visible region are observed at 670-710 and at 430-460 nm, and there are a number of charge-transfer transitions in the near-UV region. Figure 6 shows the spectrum of **8**. The nature of these transitions in the visible is not well understood; they may be charge-transfer bands associated with the nonlinear $[V\text{-O}\text{-}V]^{4+}$ group or simultaneous pair excitations or a mixture of both.[31]

The yellow compounds **9** and **10** display a series of charge-transfer bands at wavelengths <400 nm (Figure 7).
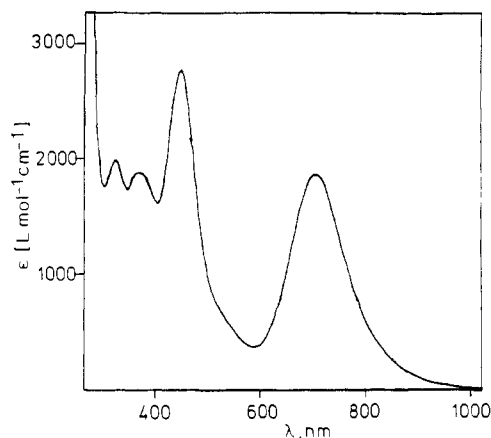
Figure 6. Electronic spectrum of **8** in CH_3CN at 20 °C.

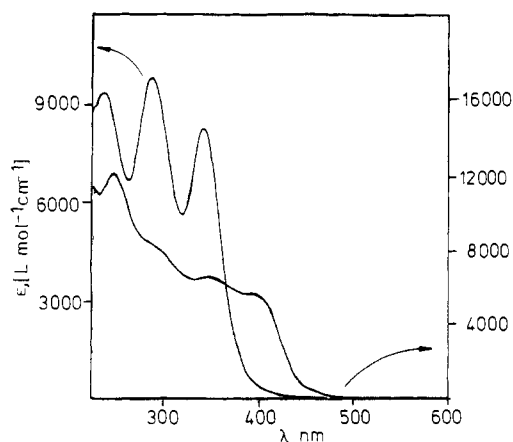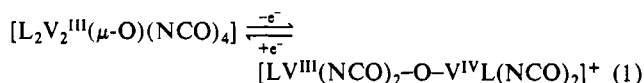**Figure 7.** Electronic spectra of **9** in CH_2Cl_2 (left-hand scale) and **10** (right-hand scale) in CH_3CN at 20 °C.

The monomeric vanadyl species **4** and **5** show the usual two weak absorption maxima in the visible region, which are d–d transitions.

Electrochemistry. The cyclic voltammograms of **5** and **6** are shown in Figure 8. Both complexes were investigated in acetonitrile solution containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte at a glassy-carbon or Au working electrode and a Ag/AgCl reference electrode. Redox potentials are referenced versus the internal standard ferrocenium/ferrocene (Fc⁺/Fc). In the potential range –2.0 to +2.0 V vs Ag/AgCl, **5** shows one reversible one-electron-transfer wave at +0.60 V vs Fc⁺/Fc, which corresponds to the couple [LVO-(NCO)₂]⁰/⁺, and an irreversible reduction at –2.45 V vs Fc⁺/Fc. Thus, **5** forms reversibly the monooxovanadium(V) species [LVO(NCO)₂]⁺ in aprotic media.

In contrast, **6** displays under identical experimental conditions in the potential range +1.5 V to –1.0 V vs Ag/AgCl *two* reversible one-electron-transfer waves ($\Delta E_p = E_{p,red} - E_{p,ox} = 60$ mV) at +0.60 V and –0.43 V vs Fc⁺/Fc. The peak current functions (cf) of both waves are different (cf values for the first and second oxidation processes are 10 and 35 μA V⁻¹/² s¹/² mmol⁻¹ L), which indicates that two different species are electroactive in solution. Since the potential at +0.60 V vs Fc⁺/Fc is identical with the one observed for **5** (see above), we assume that **6** was partially oxidized to monomeric **5**. The redox process at $E_{1/2} = -0.43$ V vs Fc⁺/Fc may then be assigned to the reversible formation of a mixed-valent $V^{III}V^{IV}$ oxo-bridged species, as is shown in eq 1.

$$[L_2V_2^{III}(\mu\text{-}O)(NCO)_4] \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}}$$
$$[LV^{III}(NCO)_2\text{-}O\text{-}V^{IV}L(NCO)_2]^+ \quad (1)$$

Very similar electrochemical behavior has been reported by Christou and co-workers[7] for [V₂O(aet)₄]·dmf (aet = 2-aminoethanethiol). Shepherd et al.[9] have obtained a mixed valent
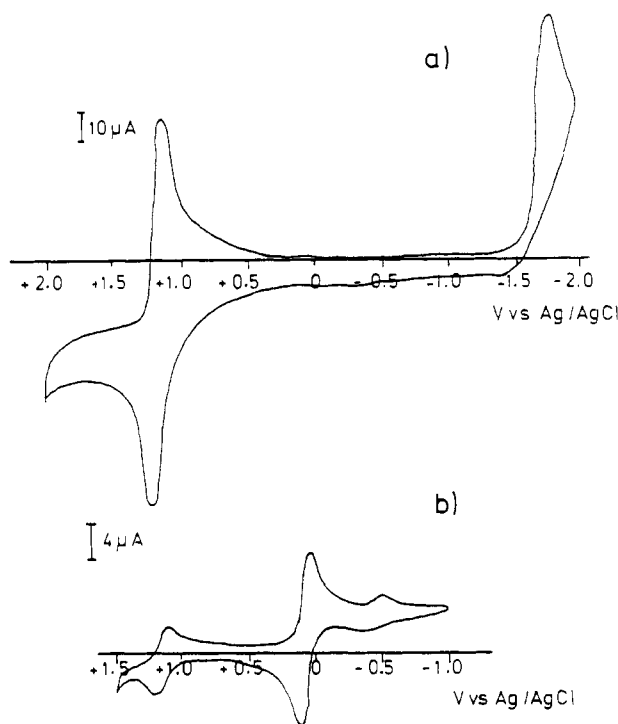
Figure 8. Cyclic voltammograms (CH_3CN; 0.1 M [*n*-Bu₄N]PF₆) of (a) **5** at an Au electrode and (b) **6** at a glassy-carbon electrode (scan rate 100 mV s⁻¹).
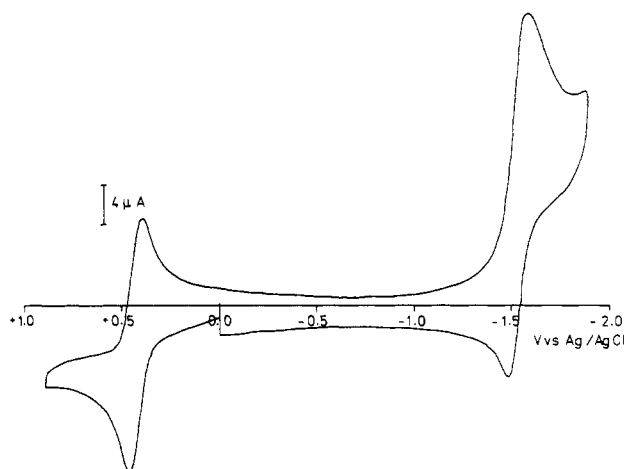
Figure 9. Cyclic voltammogram of **7** in CH_3CN (0.1 M [*n*-Bu₄N]PF₆) at an Au electrode at scan rate 100 mV s⁻¹.

$V(III)/V(IV)$ species in solution from the $[V_2^{III}O(ttha)]^{2-}$ precursor by oxidation with oxygen; the electrochemistry has also been investigated, but no reversible one-electron-transfer process has been observed.

Interestingly, the cyclic voltammogram of **7** in acetonitrile at an Au working electrode (Figure 9) exhibits reversible one-electron- and quasi-reversible one-electron-transfer waves at –0.095 and –1.805 V vs Fc⁺/Fc, which correspond to the couples $V^{IV}V^{III}/V^{III}_2$ and $V^{III}_2/V^{III}V^{II}$, respectively.
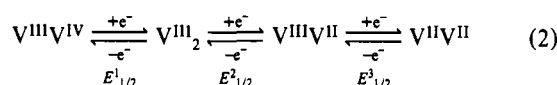
The electrochemistry of $[L_2V_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2](PF_6)_2$ has been investigated previously. In acetonitrile solution two reversible one-electron-transfer processes have been observed at –0.02 and –1.87 V vs Fc⁺/Fc, which have been attributed to the formation of $V^{III}V^{IV}$ and $V^{III}V^{II}$ mixed-valent species, respectively. The cyclic voltammogram of **8** shown in Figure 10 is similar, but at fast scan rates (>100 mV s⁻¹) a third quasi-reversible one-electron-transfer wave has been detected at very negative potentials. At slow scan rates (20 mV s⁻¹) this process becomes irreversible, indicating the instability of the highly reduced form of **8** in solution. The redox potentials $E^1_{1/2}$, $E^2_{1/2}$, and $E^3_{1/2}$ are observed at +0.20, –1.84,
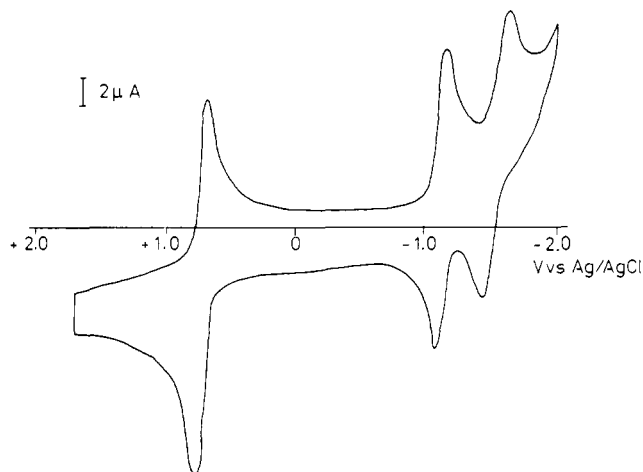
Figure 10. Cyclic voltammogram of **8** in CH_3CN (0.1 M [n-Bu$_4$N]PF$_6$) at an Au electrode at scan rate 200 mV s^{-1}.

and −2.10 V vs Fc$^+$/Fc, which correspond to the processes in eq 2.

$$V^{III}V^{IV} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} V^{III}_2 \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} V^{III}V^{II} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} V^{II}V^{II} \qquad (2)$$

$$\underset{E^1_{1/2}}{} \qquad \underset{E^2_{1/2}}{} \qquad \underset{E^3_{1/2}}{}$$

Substitution of the acetato bridges in [L$_2$V$_2$(μ-O)(μ-O$_2$CCH$_3$)$_2$]$^{2+}$ by benzoato bridges brings about an anodic shift of $E^1_{1/2}$ and $E^2_{1/2}$ by 220 and 30 mV. Similar effects have been reported for the corresponding (μ-oxo)bis(carboxylato)diruthenium(III) complexes.[32]

Summary. We have shown in this study that the octahedral monomeric complexes **1** and **2** containing the blocking tridentate macrocycle L and three labile unidentate ligands such as Cl$^-$ or CF$_3$SO$_3^-$ are hydrolyzed in aqueous solution under anaerobic conditions to form binuclear species containing the [V–O–V]$^{4+}$ core. In **6–8** the two V(III) centers are intramolecularly ferromagnetically coupled. Electrochemically these complexes may be reversibly oxidized or reduced, generating the mixed-valence V^{III}V^{IV} and V^{III}V^{II} binuclear complexes. The reaction of NH$_4$VO$_3$ or V$_2$O$_5$ with L in CH$_3$CN/H$_2$O yields the novel neutral complex **9**, which is protonated in acidic solution at the *cis*-VO$_2$ core to give the *cis*-VO(OH) unit. This reaction emphasizes nicely the analogy between the *cis*-VO$_2$ functionality and organic carboxylates.

Registry No. **1**, 112087-96-4; **2**, 123812-88-4; **3**, 123812-89-5; **4**, 123812-90-8; **5**, 123812-91-9; **5**$^+$, 123880-71-7; **6**, 123812-92-0; **6**$^+$, 123812-98-6; **7**, 123812-93-1; **8**, 123812-94-2; **9**, 123812-95-3; **10**, 123812-97-5; [L$_2$V$_2$(μ-O)(μ-O$_2$CCH$_3$)$_2$]I$_2$·2H$_2$O, 106264-13-5; [L$_2$V$_2$-(acac)$_2$O]$^{3+}$, 123834-35-5; [L$_2$V$_2$(acac)$_2$O]$^+$, 123812-99-7; [L$_2$V$_2$O-(C$_6$H$_5$CO$_2$)$_2$]$^{3+}$, 123813-00-3; [L$_2$V$_2$O(C$_6$H$_5$CO$_2$)$_2$]$^+$, 123813-01-4; [L$_2$V$_2$O(C$_6$H$_5$CO$_2$)$_2$], 123813-02-5.

Supplementary Material Available: For complexes **7**, **9**, and **10**, listings of crystallographic data, bond lengths and bond angles, anisotropic thermal parameters, and calculated positions of hydrogen atoms and their thermal parameters (11 pages); observed and calculated structure factor tables (48 pages). Ordering information is given on any current masthead page.

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Orthophosphate Complexes of Cobalt(III). *trans*-[Co(en)₂(OH₂)(OPO₃H)]ClO₄·¹/₂H₂O and Its Properties in Aqueous Solution

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trans-[Co(en)$_2$(OH$_2$)(OPO$_3$H)]ClO$_4$·¹/$_2$H$_2$O has been prepared, and its properties in aqueous solution have been investigated as a function of pH (electronic spectra ϵ (λ), 48 mol^{-1} dm^3 cm^{-1} (570 nm), 69 (359) at pH 1; ^{1}H and ^{31}P NMR spectra; acidity constants, pK_{a1} = 3.1, pK_{aq} = 6.6, pK_{a2} = 9.27). An X-ray crystallographic study of *trans*-[Co(en)$_2$(OH$_2$)(OPO$_3$H)](ClO$_4$)·¹/$_2$H$_2$O [monoclinic, $P2_1/c$, a = 13.633 (7) Å, b = 13.540 (5) Å, c = 17.331 (8) Å, β = 110.65 (4)°, Z = 8] confirms the trans orientation of the monodentate phosphato and aqua ligands. Crystal data collection 4° < 2θ < 45° at 163 K on a Nicolet P3 diffractometer gave 3900 reflections of which 1938 had I > 2σ(I). The structure was solved by Patterson methods, and weighted isotropic refinement of all non-hydrogen atoms from the two distinct molecules in the asymmetric unit converged to give R = 0.142. Kinetic and equilibrium relationships at 25 °C and 1.0 mol dm^{-3} NaClO$_4$ are as follows. (1) For reactions observed at pH <3: *trans*-[Co(en)$_2$(OH$_2$)(OPO$_3$H$_2$)]$^{2+}$ (pK_{a1} = 3.17) → *cis*-[Co(en)$_2$(OH$_2$)(OPO$_3$H$_2$)]$^{2+}$ (pK_{a1} = 3.10), k_0^t = 4 × 10^{-5} s^{-1}; [Co(en)$_2$(O$_2$P(OH)$_2$)]$^{2+}$ chelate (pK_a = −0.15) → *cis*-[Co(en)$_2$(OH$_2$)(OPO$_3$H$_2$)]$^{2+}$, k_0^{ch} = 1.67 s^{-1}. (2) For reactions at pH 3–7: *trans*-[Co(en)$_2$(OH$_2$)(OPO$_3$H)]$^+$ ⇌ *cis*-[Co(en)$_2$(OH$_2$)(OPO$_3$H)]$^+$, k_1^t = 2.08 × 10^{-4} s^{-1}, $k_1^{cis/trans}$ ∼ 0, $K_1^{trans/cis}$ ∼ 0; [Co(en)$_2$(O$_2$PO(OH))]$^+$ chelate (pK_a = 4.25) ⇌ *cis*-[Co(en)$_2$(OH$_2$)(O$_2$PO$_3$H)]$^+$, k_1^{ch} = 5.7 × 10^{-3} s^{-1}, $k_1^{cis/trans}$ = 2.2 × 10^{-4} s^{-1}, $K_1^{ch/cis}$ ≃ 0.04. (3) For reactions at pH 8–10: *trans*-[Co(en)$_2$(OH)(OPO$_3$H)] (pK_{a2} = 9.27) ⇌ *cis*-[Co(en)$_2$(OH)(OPO$_3$H)] (pK_{a2} = 9.40), k_2^t = 2 × 10^{-5} s^{-1}, $k_2^{cis/trans}$ = 1 × 10^{-5} s^{-1}, $K_2^{trans/cis}$ ≃ 0.5; [Co(en)$_2$(O$_2$PO$_2$)] chelate ⇌ *cis*-[Co(en)$_2$(OH)(OPO$_3$H)], k_2^{ch} = 2.2 × 10^{-5} s^{-1}, $k_2^{cis/ch}$ = 6 × 10^{-4} s^{-1}, $K_2^{ch/cis}$ ≃ 25. (4) For strongly alkaline conditions, pH >10: *trans*-[Co(en)$_2$(OH)(OPO$_3$)]$^-$ ⇌ *cis*-[Co(en)$_2$(OH)(OPO$_3$)]$^-$, k_3^t ≃ 1.3 × 10^{-6} s^{-1}, $k_3^{cis/trans}$ ≃ 5.4 × 10^{-6} s^{-1}, $K_3^{trans/cis}$ ≃ 4; [Co(en)$_2$(O$_2$PO$_2$)] + OH$^-$ ⇌ *cis*-[Co(en)$_2$(OH)(OPO$_3$)]$^-$, k_3^{ch} = 1.75 × 10^{-2} mol^{-1} dm^3 s^{-1}, $k_3^{cis/ch}$ = 7.5 × 10^{-5} s^{-1}, $K_3^{ch/cis}$ = 4.3 × 10^{-3} mol dm^{-3}.

Introduction

This study describes the preparation and isolation of *trans*-[Co(en)$_2$(OH$_2$)(OPO$_3$H)]ClO$_4$·¹/$_2$H$_2$O and reports its solid-state structure and its equilibrium and kinetic properties in aqueous solution over the pH range 0–12.

In a previous communication, we noted, by making use of ^{31}P NMR spectroscopy, the presence of a new species in addition to *cis*-[Co(en)$_2$(OH)(OPO$_3$)]$^-$ when alkaline aqueous solutions of

the four-membered phosphate chelate [Co(en)$_2$(O$_2$PO$_2$)] were allowed to stand at room temperature.[1] This was thought to be the trans isomer and suggested to us that opening up of the chelate under such conditions might be more complicated than was originally thought by Lincoln and Stranks.[2,3] Those authors in-

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(1) Buckingham, D. A.; Clark, C. R.; Stewart, I. *Aust. J. Chem.* **1989**, *42*, 709.